

## PROPERTIES OF Y-TYPE ZEOLITES DECATIONATED UNDER VACUUM

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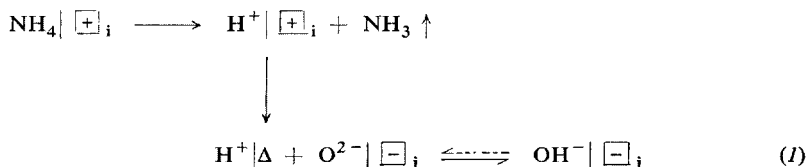
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Effect of the degree of decationation on the properties of the (H, Na)Y zeolite OH groups produced by thermal decomposition of the (NH<sub>4</sub>, Na)Y under vacuum has been studied. IR spectroscopy was used to study thermal stability of decationated zeolites. High sensitivity of the (H, Na)Y—zeolites in the hydroxyl form to adsorption and subsequent desorption of H<sub>2</sub>O, which leads to partial loss of the zeolite crystallinity, has been found. Possible influence of H<sub>2</sub>O on the (H, Na)Y zeolite is discussed.

Chemistry and structure of decationated zeolites have been already studied, but some properties of these zeolites are still under discussion<sup>1</sup>.

Greatest attention has been up to now given to Y-type zeolites produced by thermal decomposition of the ammonium form at temperatures up to 500°C, when zeolite in the hydrogen form is produced. Assuming that in the original zeolite the NH<sub>4</sub><sup>+</sup> cations occupied cationic sites of the type (*i* = I, I', II, II'), the reaction according to the Smith specification<sup>2</sup>



takes place at higher temperatures. Here, H<sup>+</sup>|Δ is proton in the interstitial site, □<sup>-</sup><sub>*j*</sub> denotes anion vacancy *j* (for Y-type zeolite, *j* = 1, 2, 3, 4). Final interaction of proton with the lattice oxygen is reversible, which is evident from the mobility of protons, demonstrated by the NMR method<sup>3</sup>. This equilibrium is dependent on temperature, presence of adsorbed molecules, geometry, and composition of the ambient around the localization centre of the proton. In aluminosilicates the equilibrium is at normal temperatures shifted towards covalently linked hydrogen, as results from some of its properties (*e.g.* noninterchangeability of H by Na<sup>+</sup> cations from a NaCl solution; however, the weakly acidic character of this hydrogen is demonstrated by a reaction with NH<sub>3</sub>, the NH<sub>4</sub><sup>+</sup> ions being thus produced)<sup>4</sup>. When studying infrared bands of structural OH groups of zeolites and behaviour of these groups in the sorption of molecules, a number of dependences have been found, some of them having no unambiguous interpretation<sup>4-10</sup>.

The present paper deals with properties of the (H,Na)Y zeolite, which was prepared by thermal decomposition of the (NH<sub>4</sub>, Na)Y under vacuum, and with its thermal stability and properties in the repeated hydration–dehydration cycle.

## EXPERIMENTAL

The zeolite samples of various NH<sub>4</sub><sup>+</sup> ions contents were prepared by ion-exchange of NaY from the NH<sub>4</sub>NO<sub>3</sub> solution at the temperature of 80°C. A higher degree of the ion-exchange was achieved by a repeated exchange with freshly prepared NH<sub>4</sub>NO<sub>3</sub> solution.

As a starting sample, the Y-type zeolite having a faujasite structure was used, of composition 0.96 Na<sub>2</sub>O.0.041CaO.Al<sub>2</sub>O<sub>3</sub>.5.04 SiO<sub>2</sub>. Compositions of the mean elementary cell of the zeolites employed are listed in Table I.

The IR spectra of transparent samples (8–14 mg/cm<sup>2</sup> thick) produced by pressing powdered zeolite under a pressure of 1000 kp/cm<sup>2</sup> were made. The spectra were obtained by means of spectrometer Perkin-Elmer 621 with use of standard program and double slit. In the path of the reference beam an attenuator was employed to correct the % *T* scale.

The samples were thermally decomposed under a vacuum of 10<sup>-6</sup> Torr in an IR cell described previously<sup>11</sup>. Powdered (NH<sub>4</sub>, Na)Y zeolite was uniformly distributed over a steel block in which a small transparent plate was pressed. The thin plate transmitting about 10% of incident radiation at 4000 cm<sup>-1</sup> was fixed in a quartz enclosure and inserted in an evacuated cell tube into a furnace. Dehydration and decomposition of the ammonium form were usually carried out at 350°C for 4 hours. The cells were provided with CaF<sub>2</sub> and KBr windows sealed by Apiezon Wax 100. Thickness of the sample was determined by weighing, prior to pressing the pellet. The X-ray diffraction was accomplished using the Debye-Sherrer method and diffractograph Chirana (Prague).

## RESULTS

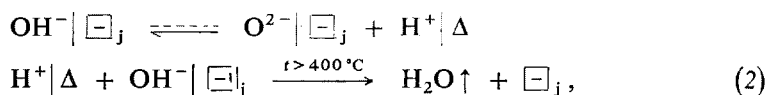
The preparation of decationated zeolites by decomposition of the (NH<sub>4</sub>)<sub>x</sub>Na<sub>1-x</sub>—Y whose composition is given in Table I, proceeded at 350°C under a vacuum of 10<sup>-5</sup> to 10<sup>-6</sup> Torr. The resulting product was checked by sorption capacity read out from the adsorption isotherm of argon at -190°C, by IR spectra, and X-ray diffraction. As follows from Table I, the sorption capacity rises linearly in the exchange of Na<sup>+</sup> cations for H<sup>+</sup>, as a result of the change in the molecular weight of zeolite. Likewise the IR spectra (Fig. 1) of zeolites of the given series display typical absorption bands of structural OH groups, described in the literature for the Y-type zeolite in the hydrogen form, namely the so-called high-frequency band (HF) at 3640 cm<sup>-1</sup> and low-frequency band (LF) at 3550 cm<sup>-1</sup>. Their intensities rise with the increasing degree of decationation of zeolites, as evident from Fig. 2. In this figure, maximum absorbances for HF and LF bands are plotted, converted to the unit zeolite thickness of mg/cm<sup>2</sup>. The band intensities are average values of 3–5 independent measurements. Owing to the overlap of bands, no integrated intensities were used. Since a certain inaccuracy may occur, the data are used for qualitative statement only. The low-intensity band at 3740 cm<sup>-1</sup>, apparent in the spectra (Fig. 1), does not change, if the

TABLE I  
Composition of the Mean Elementary Cell of the Series of Zeolites  $(\text{NH}_4)_x\text{Na}_{1-x}\text{---Y}$  and Their Sorption Capacity

Sample (abr. formula)	Analysis				Composition of ideal elementary cell	Sorption capacity mmol/g (argon)
	$\text{Na}_2\text{O}$	$\text{CaO}$	$(\text{NH}_4)_2\text{O}$	$\text{Al}_2\text{O}_3$ $\text{SiO}_2$		
$\text{Na---Y}$	0.96	0.041	---	1	$\text{Na}_{52.8}\text{Ca}(\text{AlO}_2)_{55}(\text{SiO}_2)_{137}$	10.42
$\text{Na}_{0.88}\text{H}_{0.12}\text{---Y}$	0.88	0.039	0.079	1	$\text{Na}_{48.4}\text{Ca}(\text{NH}_4)_{4.3}(\text{AlO}_2)_{55}(\text{SiO}_2)_{137}$	—
$\text{Na}_{0.81}\text{H}_{0.10}\text{---Y}$	0.81	0.035	0.12	1	$\text{Na}_{44.5}\text{Ca}(\text{NH}_4)_{6.6}(\text{AlO}_2)_{55}(\text{SiO}_2)_{137}$	10.49
$\text{Na}_{0.71}\text{H}_{0.29}\text{---Y}$	0.71	0.033	0.25	1	$\text{Na}_{39.0}\text{Ca}(\text{NH}_4)_{13.7}(\text{AlO}_2)_{55}(\text{SiO}_2)_{137}$	10.87
$\text{Na}_{0.61}\text{H}_{0.39}\text{---Y}$	0.61	0.028	0.36	1	$\text{Na}_{33.2}\text{Ca}(\text{NH}_4)_{19.8}(\text{AlO}_2)_{55}(\text{SiO}_2)_{137}$	11.20
$\text{Na}_{0.54}\text{H}_{0.46}\text{---Y}$	0.54	0.039	0.48	1	$\text{Na}_{29.7}\text{Ca}(\text{NH}_4)_{26.4}(\text{AlO}_2)_{55}(\text{SiO}_2)_{137}$	11.12
$\text{Na}_{0.43}\text{H}_{0.57}\text{---Y}$	0.43	0.021	0.57	1	$\text{Na}_{23.6}\text{Ca}(\text{NH}_4)_{31.3}(\text{AlO}_2)_{55}(\text{SiO}_2)_{137}$	11.05
$\text{Na}_{0.30}\text{H}_{0.70}\text{---Y}$	0.29	0.033	0.72	1	$\text{Na}_{16.4}\text{Ca}(\text{NH}_4)_{39.6}(\text{AlO}_2)_{55}(\text{SiO}_2)_{137}$	11.16
$\text{Na}_{0.13}\text{H}_{0.87}\text{---Y}$	0.13	0.036	0.88	1	$\text{Na}_{7.1}\text{Ca}(\text{NH}_4)_{48.4}(\text{AlO}_2)_{55}(\text{SiO}_2)_{137}$	11.24
$\text{Na}_{0.01}\text{H}_{0.99}\text{---Y}$	0.012	0.035	1.01	1	$\text{Na}_{0.6}\text{Ca}(\text{NH}_4)_{55.5}(\text{AlO}_2)_{55}(\text{SiO}_2)_{137}$	11.06

zeolite composition is changing. As has been presented elsewhere<sup>12,13</sup>, the data in question exhibit also their usual properties, *i.e.* the HF band at  $3640\text{ cm}^{-1}$  is affected by sorption of molecules of saturated as well as nonsaturated hydrocarbons, whereas the LF band does not change within the course of their sorption.

Decomposition of the  $(\text{NH}_4, \text{Na})\text{Y}$  zeolite at  $350^\circ\text{C}$  under vacuum guaranteed minimum formation of defects in the zeolite lattice, due to dehydroxylation taking place at  $t > 400^\circ\text{C}$  according to reaction



the oxygen vacancy  $\square_j$  in the  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra being produced. During

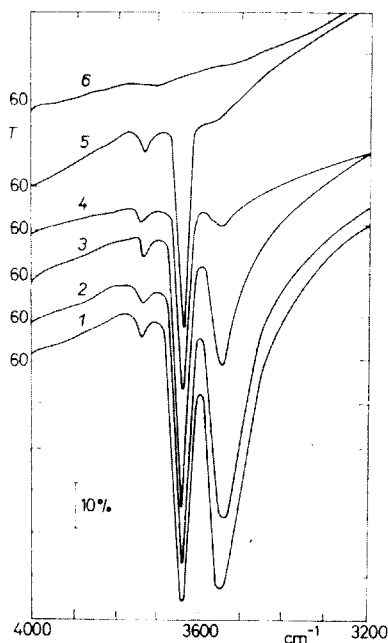


FIG. 1

Infrared  $\nu(\text{OH})$  Bands of the  $\text{H}_x\text{Na}_{1-x}\text{-Y}$  Prepared by Thermal Decomposition ( $350^\circ\text{C}$ , 4 h) of the Ammonium Form under Vacuum  
 1  $\text{H}_{0.99}\text{Na}_{0.01}\text{-Y}$ , 2  $\text{H}_{0.70}\text{Na}_{0.30}\text{-Y}$ ,  
 3  $\text{H}_{0.46}\text{Na}_{0.54}\text{-Y}$ , 4  $\text{H}_{0.29}\text{Na}_{0.71}\text{-Y}$ , 5  
 $\text{H}_{0.12}\text{Na}_{0.88}\text{-Y}$ , 6  $\text{Na}\text{-Y}$ .

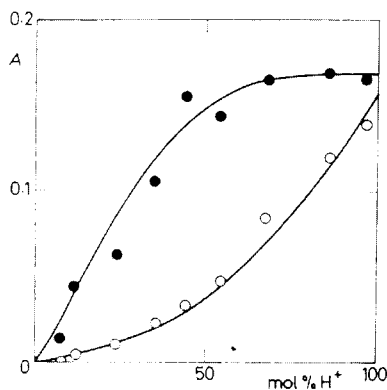


FIG. 2

Plot of Intensities of Bands HF  $3640\text{ cm}^{-1}$  and LF  $3550\text{ cm}^{-1}$  against Composition of the  $\text{H}_x\text{Na}_{1-x}\text{-Y}$

● HF, ○ LF.

the preparation of this so-called dehydroxylated form, changes in the lattice take place, which were established both by IR spectra and X-ray diffraction as well as by determining the sorption capacity. Fig. 3 shows a typical spectrum of the  $H_{0.70} \cdot Na_{0.30}$ -Y zeolite produced by decomposition under vacuum (curve 1), on activation at  $500^{\circ}\text{C}$  for 4 hours under vacuum (curve 2), and on further activation at equal temperature after 24 hours (curve 3). The spectrum is characteristic by a more rapid weakening of band at  $3550\text{ cm}^{-1}$  than of that at  $3640\text{ cm}^{-1}$ , and by intensification of band at  $3740\text{ cm}^{-1}$ . An analogous process took place, if the same zeolite was decomposed under vacuum directly at  $500^{\circ}\text{C}$  for 4 hours (Fig. 4, curve 1) and additionally activated at  $500^{\circ}\text{C}$  under vacuum for 24 hours. These zeolites had also lower sorption capacity and impaired diffraction pattern after the activation.

In order to examine questionable literature data<sup>14,15</sup> on the influence of water vapour on the (H, Na)Y zeolite, the repeated hydration of the (H, Na)Y zeolite at  $25^{\circ}\text{C}$  and subsequent desorption of adsorbed  $\text{H}_2\text{O}$  at  $350^{\circ}$  under vacuum have been studied, consequently under conditions which exclude dehydroxylation of the sample. Fig. 5 presents IR spectra of the original  $H_{0.70}Na_{0.30}$ -Y zeolite decomposed under vacuum at  $350^{\circ}\text{C}$ , and furthermore spectrum of the same sample which was overnight hydrated under atmospheric pressure by means of air humidity, and afterwards activated at  $350^{\circ}\text{C}$  under vacuum for 4 hours. A distinct increase of intensity of the band at  $3740\text{ cm}^{-1}$ , as well as marked decrease of intensities of the bands

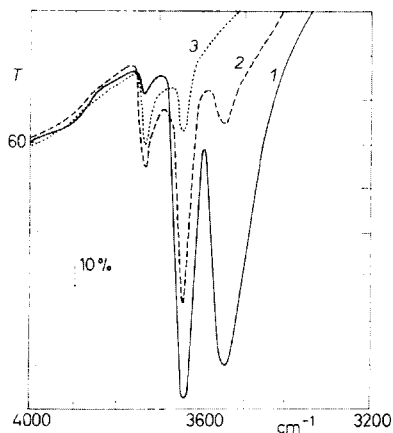


FIG. 3

Spectra of the  $H_{0.70}Na_{0.30}$ -Y

1 Original sample (vacuum,  $350^{\circ}\text{C}$ , 4 h),  
2 on activation (4 h,  $500^{\circ}\text{C}$ , vacuum), 3 on  
activation (24 h,  $500^{\circ}\text{C}$ , vacuum).

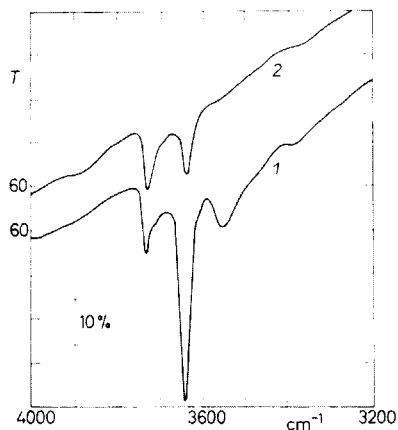


FIG. 4

Spectra of the  $H_{0.70}Na_{0.30}$ -Y

1 Decomposition ( $500^{\circ}\text{C}$ , 4 h), 2 on further  
activation ( $500^{\circ}\text{C}$ , 4 h).

at  $3640$  and  $3550\text{ cm}^{-1}$ , with its simultaneous stretching towards lower wave numbers, can be seen in the spectra. Analogous process takes place even if the (H, Na)Y zeolite is involved. The sorption capacities measured on the  $\text{H}_{0.70}\text{Na}_{0.30}\text{-Y}$  zeolite show a continuous decrease in the repeated hydration–dehydration cycle. Original sorption capacity of  $12.03\text{ mmol/g}$  decreased after 1, 2, and 3 cycles to  $10.52$ ,  $9.39$ , and  $7.35$ , respectively. X-ray diffraction of the sample after the last hydration–dehydration cycle points to an advanced amorphization of zeolite.

## DISCUSSION

The  $\text{H}_x\text{Na}_{1-x}\text{-Y}$  zeolites obtained by decomposition of ammonium form at  $350^\circ\text{C}$  under vacuum possess all typical properties of the (H, Na)Y zeolite. The spectra include a symmetric band at  $3640\text{ cm}^{-1}$  (HF) and an asymmetric one at  $3550\text{ cm}^{-1}$  (LF), whose intensities are dependent on composition of the zeolite. Band at  $3740\text{ cm}^{-1}$ , independent of composition, is as a rule assigned either to the admixture of amorphous  $\text{SiO}_2$  or to OH groups which terminate the zeolite crystal<sup>4</sup>. Our results show that with the increasing decationation, band at  $3640\text{ cm}^{-1}$ , whose increase is retarding with the rising degree of decationation, preferably increases, whereas band at  $3550\text{ cm}^{-1}$  is produced only on reaching approx. the 30% exchange of  $\text{Na}^+ \dots \text{H}^+$ , and continues increasing nearly linearly. A qualitatively consistent result was also found by Ward<sup>16</sup>, and Uytterhoeven and Jacobs<sup>5</sup>. Band at  $3640\text{ cm}^{-1}$  was proved to be produced in the decomposition of  $\text{NH}_4^+$  cations which occur in large cavities of the Y-type zeolite structure. In accordance with the diminution of cations from large cavities, even decrease of adsorption heats of molecules sensitive to a change in the electrostatic field, due to disappearance of  $\text{Na}^+$  cations<sup>13</sup>, has been established. The cations from large cavities are obviously more easily exchangeable than

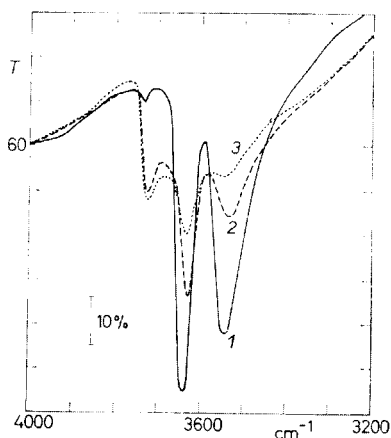


FIG. 5

Spectrum of the  $\text{H}_{0.70}\text{Na}_{0.30}\text{-Y}$

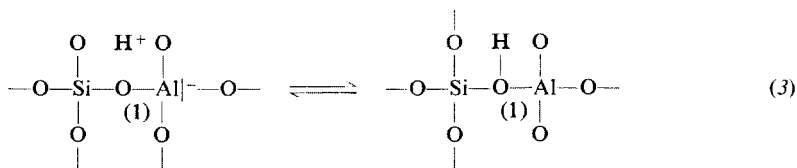
1 Sample prepared by decomposition of the ammonium form (vacuum,  $350^\circ\text{C}$ , 4 h), 2 on adsorption ( $25^\circ\text{C}$ , 12 h) and desorption of  $\text{H}_2\text{O}$  (4 h,  $350^\circ\text{C}$ , vacuum), 3 on repeated hydration and dehydration.

cations of the sodalite units. Protons produced by reaction (1) are therefore localized in large cavities, but the fact, whether they are localized in large cavities with oxygen  $O_{(1)}$  or  $O_{(3)}$  is up to now questionable<sup>6-8,17,18</sup>.

Unlike this, the LF band corresponds to the formation of hydroxyl groups which behave differently from the OH groups of band  $3640\text{ cm}^{-1}$ . They are insensitive to the sorption of nonpolar molecules and alkenes. In accordance with Uytterhoeven and coworkers<sup>19</sup> we assume that although these hydrogens are more loosely bound, they do not react with adsorbed molecules because of their localization in non-accessible sodalite units. The change in their vibration may then occur only as a result of a strong perturbation, for example, by polarization of the lattice during sorption of a molecule with a large dipole moment, or as a result of interaction with an adsorbed basic molecule after replacement into the accessible position<sup>19</sup>.

Delocalization of protons, as has been presented in equation (1), depends on the surroundings of the localization centre in the lattice, and temperature. Ward showed<sup>16</sup> that frequency of stretching vibrations both for the HF and LF bands decreases with the increasing temperature, this corresponding to the rise in lability of the OH bond. Nuclear resonance confirmed also the increased frequency of jumping of protons with increasing temperature<sup>3</sup>. The fact that by treatment under vacuum the band of the lowest wave numbers, *i.e.* LF, disappears, is in agreement with the assumption that the most labile OH groups are most readily removed. From this point of view thermal stability of the band at  $3740\text{ cm}^{-1}$  may also be understood.

The zeolite lattice is assumed to have cations and in the H-form also hydrogens localized at  $AlO_4$  oxygens. Certain ionicity of the hydrogen bond to the lattice oxygen can be formally expressed by equilibrium



The coordinatively unsaturated Al may thus become the Lewis acidic centre. It is possible that also adsorbed water on the (H, Na)Y zeolite can enter interaction with this centre and causes weakening of bond  $O_1 \dots Al$ . At the temperatures of  $t > 300^\circ\text{C}$  a complete break of the  $O_1 \dots Al$  bond takes place in the course of desorption, which becomes evident by partial destruction of the zeolite lattice and in the IR

spectra by an increase of the band intensity of terminal  $-\text{Si}-\text{OH}$ , *i.e.* of the band at  $3740\text{ cm}^{-1}$ . The conception of the somewhat more labile bond of  $O_{(1)}$  in the zeolite lattice is in agreement with the finding<sup>20</sup> that in the dehydroxylation of zeolite, the occupation factor of the  $O_{(1)}$ -type oxygens decreases. On the contrary, sorption

of strongly basic molecules ( $\text{NH}_3$ , pyridine) shifts equilibrium (3) towards ionic structure ( $\text{NH}_4^+$ ,  $\text{PyH}^+$ , which can be proved in the IR spectrum, are being produced), which leads<sup>21</sup> to stabilization of the (H, Na)Y zeolite lattice. Recently it has been found<sup>22-24</sup> that a certain similarity exists in the behaviour of the OH groups represented by the band at  $3740\text{ cm}^{-1}$  and the  $\text{—Si—OH}$  groups belonging to amorphous  $\text{SiO}_2$ , and that assignment of band at  $3740\text{ cm}^{-1}$  to  $\text{—Si—OH}$  is adequate. Owing to the fact that in amorphous aluminosilica gel only band at  $3750\text{ cm}^{-1}$  is observable<sup>23</sup>, presence of the band at  $3740\text{ cm}^{-1}$  seems conceivable as indication of the amorphization of zeolite, during which number of terminal  $\text{—Si—OH}$  groups increased.

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